

Ultrafast Laser Inducing Continuous Periodic Crystallization in the Glass Activated via Laser-Prepared Crystallite-Seeds

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Tailoring ultrafast light–matter interaction as an enabler to create functional periodic crystalline patterns inside transparent dielectrics is of great scientific and technological significance but remains a tremendous challenge because of plenty of unclarified process details and physical mechanisms. Here, a dynamic process of ultrafast laser-induced continuous periodic crystallization (CPC) to generate self-organized crystal arrays (CAs) inside the glass is reported. The crystallite-seeds induced by ultrafast laser are revealed to offer an auxiliary effect that can initiate and maintain the CPC process, which promises the high-efficiency writing of CAs. The auxiliary effect originates from photo-induced defects in the crystallite-seeds, functions by drastically decreasing the pulse energy threshold for writing CAs, and can be manipulated by tuning the glass compositions and laser parameters. The created CAs are erasable and rewritable, which allows for potential applications in optical information encryption and data storage. This work not only opens up an avenue for creating embedded periodic crystalline patterns with extremely high efficiency but also helps to clarify the dynamics of ultrafast laser nanostructuring inside transparent dielectrics.

elements and attracted extensive research interest in recent years.^[1–5] In particular, ultrafast laser direct writing based glass-crystal optics has been widely reported to realize 3D nonlinear photonic crystals,^[6,7] second harmonic generation,^[8,9] optical waveguides,^[10,11] and perovskite quantum dots in the glass.^[12,13] However, the reported ultrafast laser-patterned microstructures mainly rely on direct laser energy deposition, and the processing precision and efficiency are very limited. Recently, functional crystal arrays (CAs) with periodically varied optical properties and nanoscale feature sizes have been demonstrated to possess promising applicable prospects in frontier studies,^[14,15] but remain very difficult to be obtained with conventional technologies. Therefore, novel approaches for realizing high-resolution periodic nanopatterning in transparent dielectrics are highly desirable to solve these problems.

1. Introduction

Selectively modifying transparent materials to create functional structures by using an ultrafast laser has become an effective, facile, and economic method to achieve advanced photonic

Extensive studies have demonstrated that periodic field distribution (PFD) generated by ultrafast laser-matter interaction process can periodically modify transparent media at the nanometer-scale level and generate polarization-dependent grating structures with a periodic change in component, accompanied with strong polarization-dependent birefringence.^[16–18] Such modification breaks the diffraction limit and is applicable to several transparent dielectrics like silica glass, borosilicate glass, and GeO₂ glass,^[19–21] which provides a highly promising approach to create CAs. However, despite nearly 20 years of study and a large number of published works, only a very limited number of materials are able to support the formation of CAs and the reason remains a mystery.^[22–24] The mechanism bridging PFD and CAs remains largely unclarified. From these studies, we note two key points. First, the formation capability of crystalline grating structures strongly depends on the thermal effect and the glass composition, which is in line with the capability of phase transition from glass to ceramic. Second, the crystal nucleus is generally a critical starting unit for crystal formation and growth.

Here, we present an ultrafast laser-induced CPC process in the La₂O₃–Nb₂O₅ glass (LN glass) that allows creating periodic structures made of self-assembled CAs. We reveal that this CPC process is catalyzed by the local defective crystallite-seeds that can offer a unique auxiliary effect to activate and

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maintain the CPC. The working principle of the auxiliary effect is featured by decreasing of energy threshold for triggering the CPC process, which is attributed to defect centers generated during the laser-induced local crystallization process. The generality of the principle of this technique allows for efficiently producing similar structures in other glass systems. Furthermore, we demonstrate the applications of the CPC in optical memory and information encryption. This work reveals that the mechanism of ultrafast laser-induced high-efficiency periodic crystallization inside glasses augments ultrafast light-matter interaction physics, and opens up an avenue for glass-based optical data storage.

2. Results and Discussion

Generally speaking, the formation of CAs in LN glass cannot be induced by using a conventional laser direct writing method. Here, we propose a scanning strategy that can enable the formation of periodic structures in glass by simply introducing crystallite-seeds with a static pre-irradiation for some time in the line path before scanning (Figure S2a, Supporting Information). In fact, not only at the starting point, the pre-irradiation induced crystallite-seeds with an injection of enough number of pulses located anywhere along the laser scan path can trigger the CPC process in the subsequent line writing (Figure 1a),

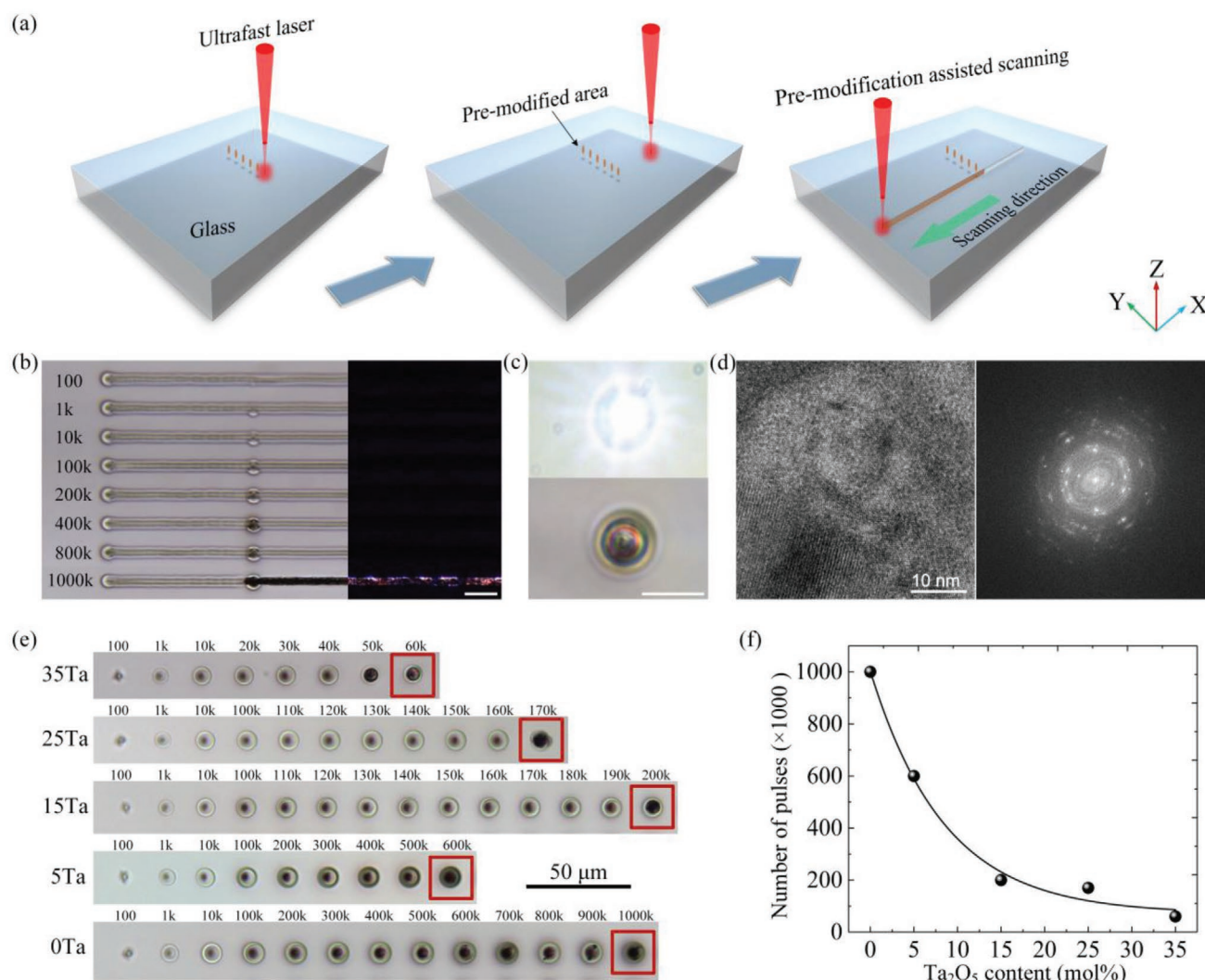


Figure 1. a) Schematic diagram of the crystallite-seeds assisted ultrafast laser direct writing process in a transparent material. The crystallite-seeds creation by static irradiation of ultrafast laser (left), the start of laser direct writing (middle), and the end of laser direct writing (right). b) Optical micrograph of the lines written with the assistance of the crystallite-seeds that are created with different incident pulse numbers (left). Birefringence image of the same region between cross polarizers (right). Scale bar: 15 μm . c) Criterion for evaluating the effectiveness of the crystallite-seeds for the CPC process. Visible white light radiation (up), and punctate aggregate precipitates (down). Scale bar: 5 μm . d) High-resolution transmission electron microscopy (HRTEM) image (left) and corresponding fast Fourier transform image (right) of the precipitates in the pre-irradiated zone. e) The evolution process of the crystallite-seeds with various incident pulse numbers and Ta_2O_5 contents. f) Dependence of the required incident pulse number on the effective crystallite-seeds on the Ta_2O_5 contents in the samples. The black line is a fitted curve with an exponential function.

leading to the generation of CAs. This is confirmed by detecting the birefringence signal.^[25] Thus, except for the PFD, the ultrafast laser-induced crystallite-seeds are also indispensable for starting the CPC process. We infer that there may be a key step that mediates the PFD to form the CPC, namely, an auxiliary effect caused by the crystallite-seeds. By using the pulse-controlled laser in-situ irradiation, pre-modified zones with different features can be obtained, and in this way, the auxiliary effect can be clearly characterized by scanning the laser through the pre-modified spots. This can offer important information for understanding the mechanism of the laser-induced CPC process.

As shown in Figure 1b, microscopic observation of pre-modified spots assisted scanning confirms that the crystallite-seeds generated with enough incident pulses can activate the subsequent CPC process. Obvious periodic birefringence signals can be detected in the lines written with different polarizations (Figure S2b, Supporting Information), indicating the presence of polarization-dependent structures. Scanning electron microscopy (SEM) observation further reveals the periodic morphology of the CAs in the laser direct writing path (Figure S2c, Supporting Information). The period of the CAs is ≈ 500 nm and the feature size of the regularly precipitated crystal pattern is only 200–300 nm. The crystal nature of the CAs is confirmed by transmission electron microscopy (TEM) (Figure S2d, Supporting Information). Notably, in the LN glass, the required pulse number for producing effective crystallite-seeds that can trigger the CPC process is at a million level. Repeated experiments show that an important criterion for evaluating the effectiveness of the pre-modification for scotting the CPC process is the appearance of punctate aggregate precipitates (Figure 1c) accompanied by the appearance of intense visible light radiation. The precipitates are further proved to be crystallites (Figure 1d). Therefore, we speculate that effective pre-modification strongly depends on the crystallization of the glass. If this is correct, adding a promoter into the glass to enhance the crystallization ability of glass systems could be an effective approach to reduce the pulse number threshold for CPC generation. To validate this speculation, the relationship between the crystallization tendency of the glass and the required pulse number for effective pre-modification is studied. Studies have shown that the crystallization tendency of LN glass can be adjusted by introducing Ta_2O_5 and the glass-forming ability greatly decreased with Ta_2O_5 substituting Nb_2O_5 .^[26,27] Here, a series of glass samples with the composition of $35\text{La}_2\text{O}_3-x\text{Ta}_2\text{O}_5-(65-x)\text{Nb}_2\text{O}_5$ (where $x = 0, 5, 15, 25$, and 35 mol%, and samples are denoted as 0Ta, 5Ta, 15Ta, 25Ta, and 35Ta glass, respectively) were prepared. Then, the auxiliary effect assisted ultrafast laser direct writing is carried out in these glasses. As illustrated in Figure 1e, introducing Ta_2O_5 to the glass significantly reduces the threshold number of pulses for the creation of effective pre-modification. The threshold pulse number for the 35Ta glass is only 6% of that for the 0Ta glass. Further analysis indicates that the threshold pulse number decreases exponentially with the increase of the Ta_2O_5 concentration (Figure 1f), which preliminarily substantiates that the activation of the auxiliary effect is strongly promoted by the crystallization behavior of the glass.

We examined the connections between the ultrafast laser-induced crystallite-seeds and the CAs. As shown in Figure 2a, the optical morphology of the pre-modified zone significantly shifts only when the number of incident pulses exceeds the threshold for creating crystallite-seeds. Corresponding Raman spectroscopy reflects this structural variation. The Raman spectra of the area irradiated with incident pulses less than 180k remain the same as that of the glass phase. However, when the incident pulse number reaches 180k, several new Raman peaks emerge, which is highly consistent with the Raman spectrum of the CAs (Figure 2b). Figure 2c further indicates that such crystallite-seeds can activate the CPC process. From the microscopic side view of a scanning line passing through a crystallite-seed, we can clearly see the significant structural transformation from glass to the CAs (Figure 2d).

As illustrated in Figure 2e, compared with the background Raman signal of the glass matrix, the Raman spectrum of the laser-induced crystallite-seeds can be characterized by three characteristic peaks ($136, 460, 712\text{ cm}^{-1}$). Specifically, the peak at around 137 cm^{-1} is associated with ionic motion and $\text{Ta}_x\text{O}_y^{z+}$ clusters, and the peaks at 460 and 712 cm^{-1} are attributed to the stretching mode of O-3Ta (triple-coordinated oxygen) in the O-Ta-based crystal matrix.^[28–30] The HRTEM observation further shows that the interlayer spacing between adjacent lattice fringes in the crystal region is 0.336 nm (Figure S2e, Supporting Information), corresponding to the Ta_2O_5 ($-1\ 0\ 5$) crystal face. Combined with the results of micro-Raman measurement, we speculate that the precipitates contain a certain amount of Ta_2O_5 (More analysis about the precipitates are found in the Supporting Information). As expected, the micro-Raman mapping images of the three characteristic peaks in the laser modified area show remarkable periodicity (Figure 2f), and the period is in line with that of the CAs. These results confirm that the laser-induced crystallite-seeds generated in the pre-modified zone have the same structure as that in the CAs, which supports that the crystallite-seeds not only activate the CPC process at the start point but also participate in the formation process of the CAs. In detail, the ongoing CPC process in the focal area can be greatly promoted by the presence of a neighboring irradiated zone, which is equivalent to the pre-induced crystallite-seeds. To further confirm this point, we introduce a spatial breakpoint in the writing path (Figure S3a, Supporting Information). As shown in Figure S3b, Supporting Information, the black circular region is a breakpoint in the glass matrix, and once the laser passes through the breakpoint, the birefringence signal immediately disappears, which proves that without the crystallite-seeds generated by the laser irradiation in the neighboring region, the CPC process is not sustainable. In other words, with the assistance of neighboring crystallite-seeds, the CPC works like a chain-reaction style process that proceeds in a domino-like manner and leads to the formation of CAs in the whole writing line.

A series of control experiments were performed to understand the working mechanism of the auxiliary effect. As shown in Figure 3a, the threshold of pulse energy for triggering the CPC process in the 25Ta glass greatly reduces from ≈ 1.0 to $\approx 0.6\ \mu\text{J}$ when there are pre-induced crystallite-seeds in the beam writing path. As pulse energy is the primary factor in exciting multi-photon ionization and multi-photon ionization is

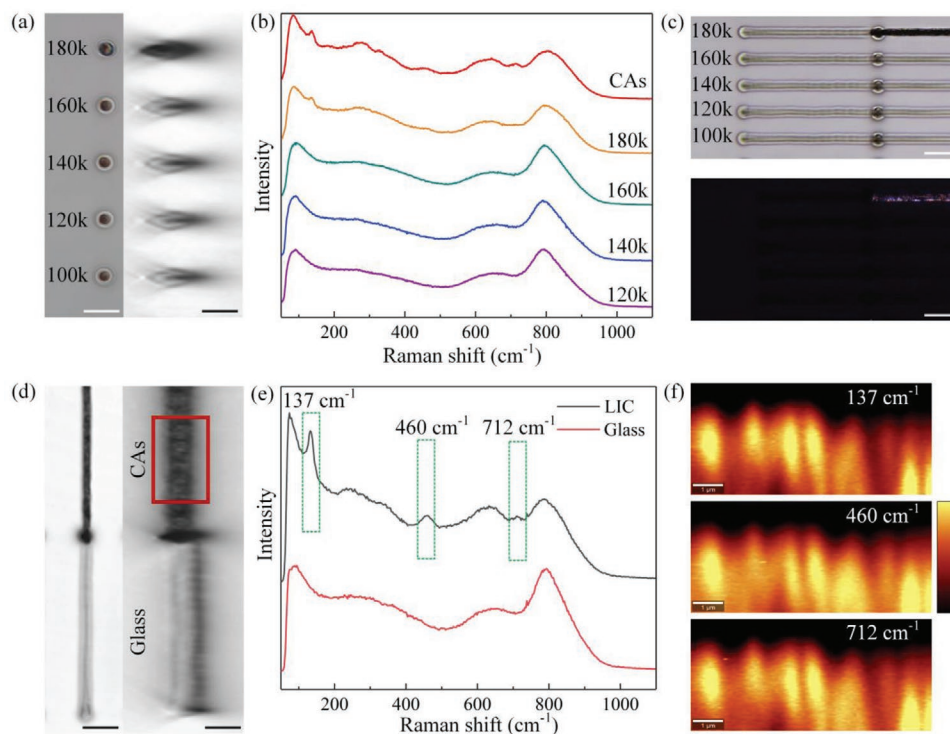


Figure 2. a) Optical micrographs of the top view (left) and side view (right) of the laser modified area with various incident pulses in 25 Ta glass. Scale bar: 10 μm . b) Raman spectra of the laser modified area with different incident pulses. c) Auxiliary effect activation test using the pre-modified spots with different incident pulses. Optical micrograph (up) and birefringence image (down). Scale bar: 10 μm . d) Optical micrographs of a scanning line written through a pre-modified point. Top view (left) and side view (right). The red box indicates the region for Raman mapping. Scale bar: 10 μm . e) Comparison of Raman spectra between the glass and the laser-induced crystallite-seeds (denoted by LIC). The green dashed boxes show characteristic Raman peaks. f) Raman spectral mapping of the characteristic Raman peaks of the CAs in the side plane. Color bar illustrates the signal intensity. Scale bar: 1 μm .

the essential condition for the establishment of the PFD,^[31] pre-induced local crystallization promotes the CPC process by significantly reducing the pulse energy threshold of multi-photon ionization. In stark contrast, Figure 3b shows that the repetition rate threshold for triggering CPC remains the same as 150 kHz whether or not crystallite-seeds are pre-induced in the writing path, indicating that the auxiliary effect has no impact on the repetition rate threshold. In other words, a repetition rate above the threshold is a prerequisite condition for activating the auxiliary effect. Namely, heat accumulation is always necessary for maintaining CPC in the line writing process.^[32]

Since laser pulse duration influence both multi-photon ionization and heat accumulation, to verify the conclusion derived from the pulse energy and the repetition rate tests above, the dependence of the auxiliary effect on pulse duration was studied with constant pulse energy. Figure 3c illustrates that when the pulse duration is shorter than 750 fs, no periodic structures are produced whether or not there are pre-generated crystallite-seeds in the writing path, indicating that the lower limit of pulse duration for activating the auxiliary effect is unaffected. This is in line with the aforementioned fact that heat accumulation is critical for the CPC process. The upper limit of pulse duration for writing CAs is ≈ 5 and 2 ps with and without the pre-generated crystallite-seeds, respectively (Figure 3d). Although peak power density is much lower when the pulse

duration is 5 ps, the pre-induced crystallite-seeds provide an auxiliary effect by significantly reducing the threshold of peak power density for multi-photon ionization, allowing the PFD to create the periodic CAs.

More interestingly, although the required pulse number for inducing effective local crystallization can be up to a million, the CPC process can still be achieved by a line scanning with an extremely high speed (up to 7000 $\mu\text{m s}^{-1}$) as long as the auxiliary effect is activated (Figure S4a, Supporting Information). Our experiments show that the CPC process can be induced with a pulse density range of 21–150 pulse μm^{-1} and the smallest pulse number density in the CPC process is strikingly only $\approx 0.01\%$ of that for creating the crystallite-seeds (Figure S4b, Supporting Information), which allows high efficiency for the large-area fabrication of periodic crystalline structures.

Although we have confirmed that crystallization is essential for the auxiliary effect, not all types of crystallization can activate the auxiliary effect. For instance, the randomly distributed crystallites formed during the glass preparation process are not able to generate a similar auxiliary effect that allows the CPC (Figure S5, Supporting Information). These observations raise a critical question: why the ultrafast laser-induced crystallization can activate the CPC process?

To reveal the origin of the auxiliary effect on the CPC, electron paramagnetic resonance (EPR) measurement is performed

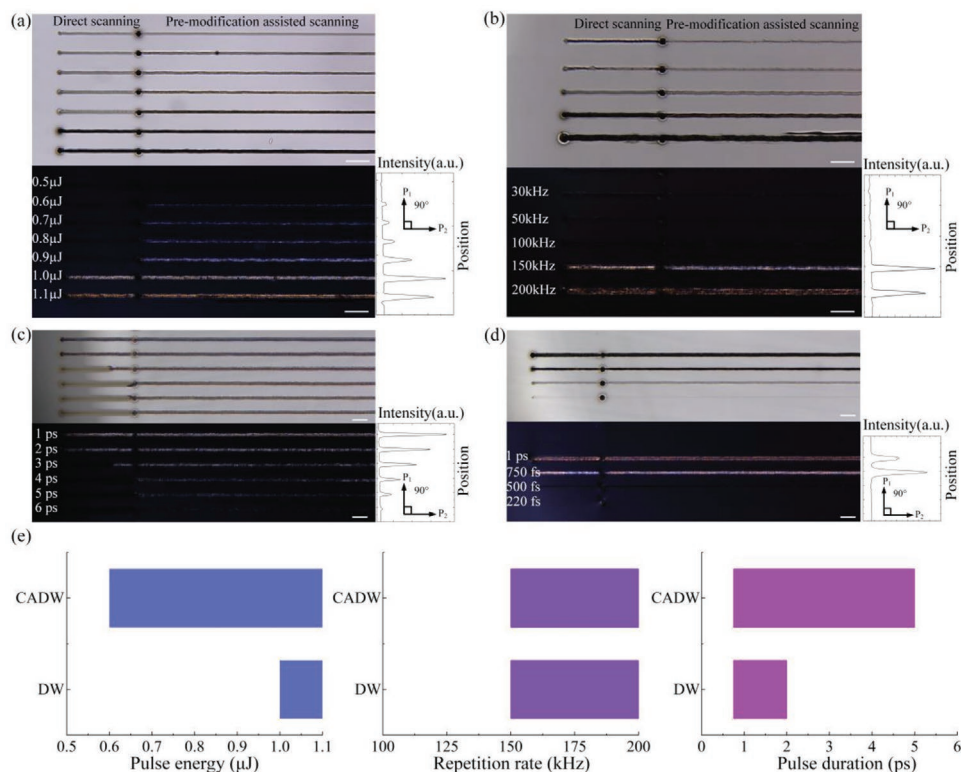


Figure 3. Comparison of pulse energy thresholds (a) and repetition rate thresholds (b) for triggering the CPC process between the laser direct scanning and the crystallite-seeds assisted scanning. Comparison of the upper limit (c) and lower limit (d) of pulse duration for activating the CPC process between the laser direct scanning and the crystallite-seeds assisted scanning. e) Process windows with respect to the pulse energy, repetition rate, and pulse duration for triggering the CPC process. CADW indicates the crystallite-seeds assisted direct writing and DW indicates the direct writing method. Scale bar: 20 μm .

to examine the inner structural properties of the laser-irradiated area. **Figure 4** (inset) shows the EPR spectra of the pristine glass and ultrafast laser modified sample where a newly emerged EPR signal is detected. The g factor of the photo-induced defects in the laser modified area can be calculated from the equation of $h\nu = gH\beta$, where h is the Planck constant, ν is the frequency of microwave, g is g factor, H is the magnetic field and β is the Bohr magneton. Accordingly, the g factor is determined to be ≈ 2.00363 , which is larger than that of the free electrons ($g_e = 2.00232$), indicating the formation of hole-type defects within the ultrafast laser irradiated area.^[33] Here, the broad EPR resonance near $g \approx 2$ originates from the holes trapped at O^{2-} ion, which generates O- hole-trapped defect centers usually created by ionizing radiation in oxide materials.^[34–36] As a consequence, the laser-induced defects reduce the bandgap of the laser modified area and make it much easier to be re-excited by subsequent incident pulses, which is in good agreement with the observed decrease of threshold pulse energy for triggering the CPC process. Meanwhile, the large number of defects serves as scattering centers, leading to much stronger interference, which is favorable for building PFD and generating periodic structures in the writing path.^[37–39] These experimental results confirm that the auxiliary effect is supported by laser-induced defective crystallites.

As shown in Figure 4, the mechanism for the auxiliary effect from crystallite-seeds for achieving the CPC process

is presented. In the focal area, ultrafast laser irradiation is performed to generate local crystallization in the glass matrix, where a relatively long pulse duration and a higher repetition rate are applied for heat accumulation. The free electrons excited by ultrafast laser are soon captured by the surrounding lattice, forming a large number of defects that can greatly promote subsequent energy absorption. When the ultrafast laser focus passes through the highly defective crystallization area, the electrons in defects can be easily excited to the conduction band, enabling the laser-induced avalanche ionization process.^[40,41] Then, the interference between the incident light and scattered waves from the plasmas generated by the multi-photon ionization causes a periodic distribution of the temperature field.^[42] Finally, the phase separation in the laser-irradiated path is gradually developed, resulting in the formation of the CAs. In this regime, native defects and inhomogeneities in glass networks are not responsible for creating periodic structures, instead, the laser-induced defective crystallites play a decisive role in the formation of periodic structures, which is different from the previous proposals that inner periodic structures induced by ultrafast laser are mediated by randomly distributed intrinsic defects in the glass matrix.^[43,44] Taken together, our results reveal that the actively induced defective crystallites are responsible for creating a strong auxiliary effect that mediates the CPC in the beam writing process.

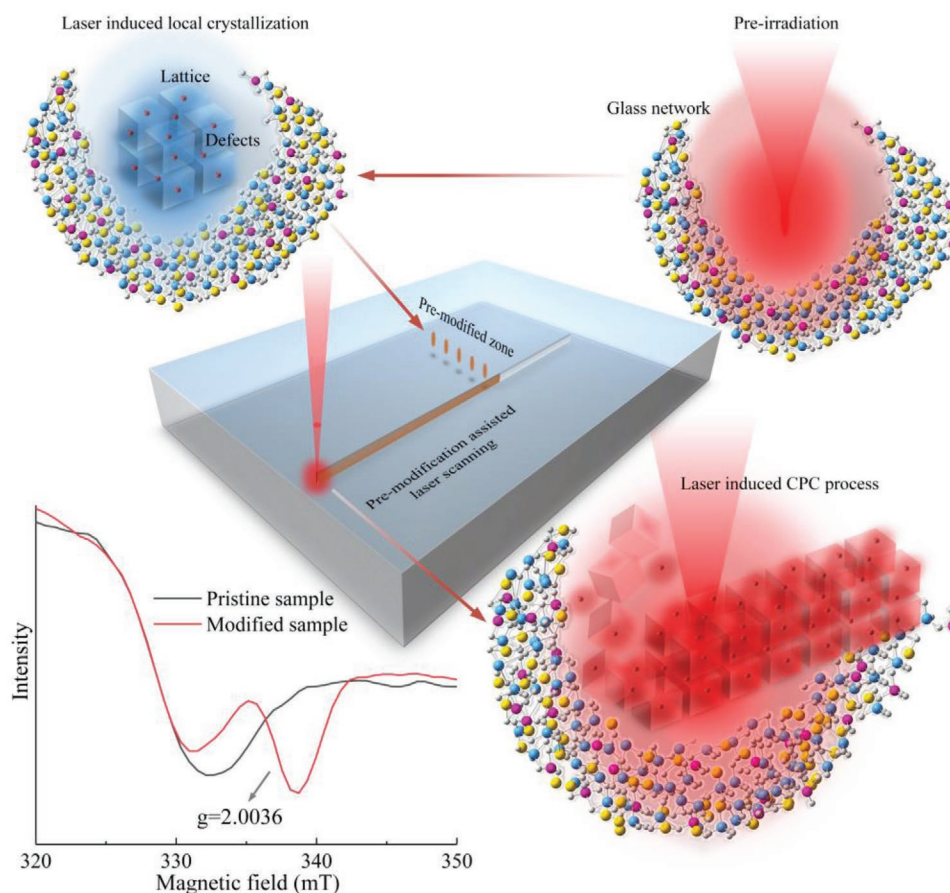


Figure 4. Schematic diagram of the auxiliary effect. Inset: EPR spectra of the laser modified sample and pristine sample.

The ultrafast laser-induced CPC and similar periodic CAs were also achieved in other glass systems. Figure S6, Supporting Information, shows the presence of artificial periodic birefringence in $\text{La}_2\text{O}_3\text{--TiO}_2$ system, $\text{La}_2\text{O}_3\text{--Al}_2\text{O}_3$ system, and $\text{La}_2\text{O}_3\text{--WO}_3$ system, which confirms that the CPC process can also be successfully activated in these media. As laser-induced crystallization and PFD are common phenomena in the glasses, our work possesses universal significance. As an evidence, dispersed nanometer-scale crystallites have recently been observed in femtosecond laser-induced grating structures inside fused silica,^[45] which can be regarded as an incomplete CPC process because the crystallization tendency of silica glass is much weaker. Given these results, the concept of ultrafast laser-induced CPC is extended to be a general strategy, which may be applied to create various functional periodic crystalline patterns in large numbers of dielectrics.

The CPC based ultrafast laser patterning in the glass is in its early stage of the investigation, and many of its properties are yet to be exploited. One of its key intriguing properties of the CAs is the polarization-dependent birefringence, which prompts us to explore their novel applications, such as data storage and encryption.^[46–48] Figure 5a presents that the birefringence signal of the CAs originally written by a 45° polarized laser can be replaced by an additional scan with a 0° polarized ultrafast laser, which verifies that the fabricated

CAs can be selectively erased and rewritten. Birefringence intensity mapping confirms that such a signal variation possesses considerably high contrast, which can be used for information encryption.

To further demonstrate the possibility of information storage and encryption by the ultrafast laser-induced CPC process, two types of digital letters are constructed inside glass by ultrafast laser writing with different polarizations (0° and 45°), respectively (Figure 5b, c). The initial code, for example, “8888”, can be changed to “2019” and “2020” by selectively rewriting specific segments with two differently polarized lasers to modulate the birefringence signal, respectively. The images of two digital letters look the same under normal white light irradiation but the decrypted information can be read out by detecting the birefringence signal of the encrypted area between cross polarizers. The code can also be quickly reset by the laser direct erasing process. Notably, as the rewriting process is operated in the area already crystallized, no additional pre-irradiation is needed, which promises an increase in encryption efficiency. Even for the first writing process in blank samples, once the local crystallization is generated, no static irradiation is needed in the following writing process due to the auxiliary effect. Furthermore, by introducing crystallization promoters like Ta_2O_5 or TiO_2 to the glass, the pulse number can be significantly reduced, which makes the ultrafast laser-induced CPC much more efficient.

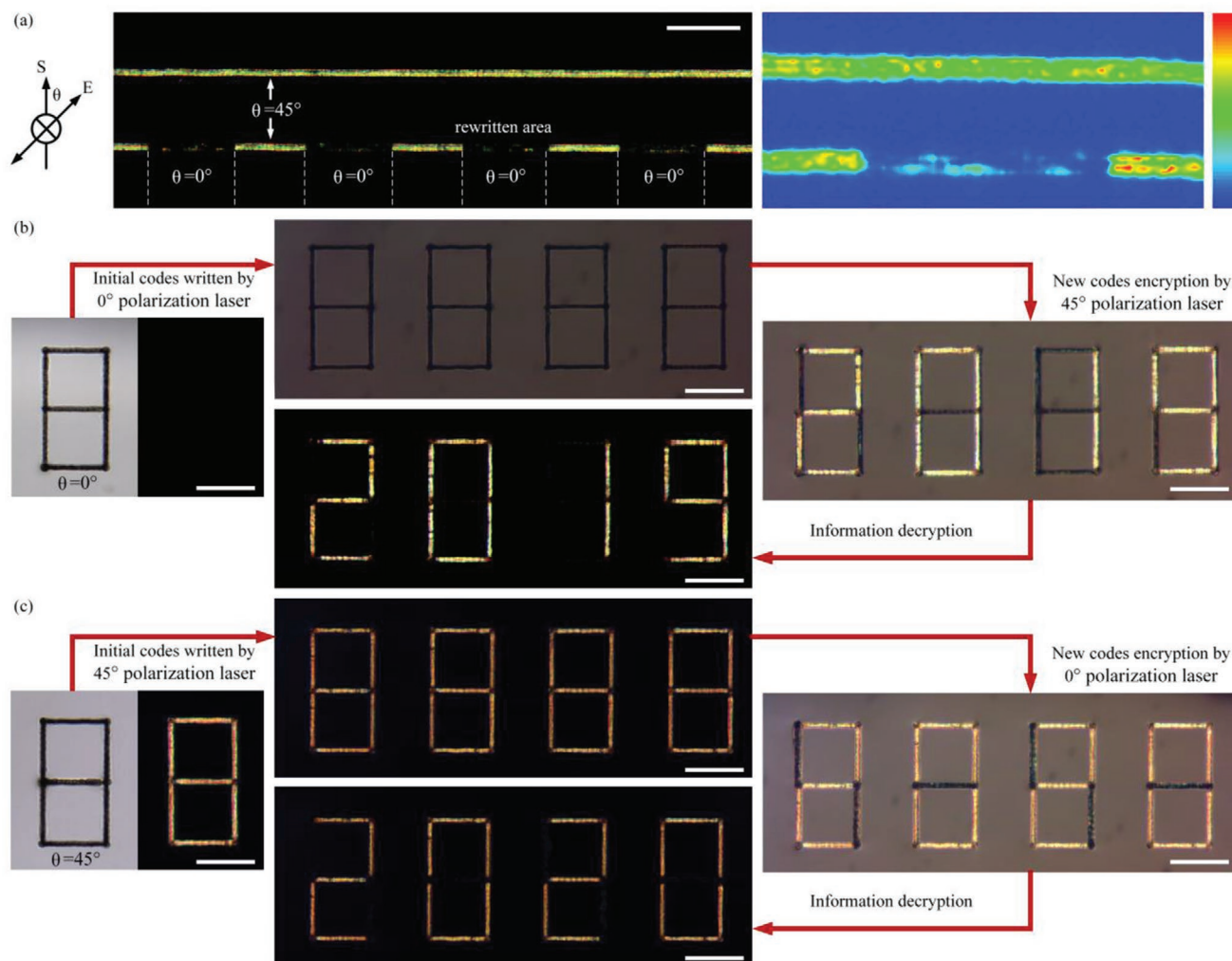


Figure 5. Demonstration of data storage and encryption. a) Birefringence image of the rewriting process of the CPC (right) and corresponding birefringence intensity mapping (left). Color bar indicates the birefringence intensity. b,c) Data encryption by rewriting the original codes with new polarization at 45° to the original polarization. Laser polarization direction is indicated by E and scanning direction is indicated by S and laser polarization is indicated by θ . Scale bar: 20 μm .

3. Conclusion

In summary, we present a method of ultrafast laser-induced CPC process to efficiently fabricate polarization-dependent periodic CAs in the glass matrix. The auxiliary effect offered by the actively induced crystallite-seeds plays a decisive role in the formation of the CAs. With this auxiliary effect, the pulse density threshold for the CPC process can be 10 000times lower than that for the conventional laser-induced crystallization, which allows for high processing efficiency. We confirmed that the laser-induced defective crystallites are the essential causes of the auxiliary effect. As the birefringence signal of the laser-induced CAs is erasable and rewritable, we further demonstrate the possibility of the applications of the CPC for information storage and encryption. Our methodology can be broadly extended to other functional glass systems, enabling the efficient fabrication of a series of novel functional photonic structures that may find potential applications in fields like optical data storage, diffractive elements, and nonlinear optics.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

auxiliary effect, continuous periodic crystallization, glass, optical data storage, ultrafast laser

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- [1] T. Will, J. Guan, P. S. Salter, M. J. Booth, *Opt. Express* **2020**, 28, 28006.
- [2] J. Cao, M. Lancry, F. Brisset, L. Mazerolles, R. Saint-Martin, B. Pommellec, *Cryst. Growth Des.* **2019**, 19, 2189.
- [3] A. Ródenas, M. Gu, G. Corrielli, P. Paiè, S. John, A. K. Kar, R. Osellame, *Nat. Photonics* **2019**, 13, 105.
- [4] D. Tan, K. N. Sharafudeen, Y. Yue, J. Qiu, *Prog. Mater. Sci.* **2016**, 76, 154.
- [5] A. Nishii, K. Shinozaki, T. Honma, T. Komatsu, *J. Solid State Chem.* **2015**, 227, 145.
- [6] S. Liu, K. Switkowski, C. Xu, J. Tian, B. Wang, P. Lu, W. Krolikowski, Y. Sheng, *Nat. Commun.* **2019**, 10, 3208.
- [7] S. Keren-Zur, T. Ellenbogen, *Nat. Photonics* **2018**, 12, 575.
- [8] D. Wei, C. Wang, H. Wang, X. Hu, D. Wei, X. Fang, Y. Zhang, D. Wu, Y. Hu, J. Li, S. Zhu, M. Xiao, *Nat. Photonics* **2018**, 12, 596.
- [9] T. Xu, K. Switkowski, X. Chen, S. Liu, K. Koynov, H. Yu, H. Zhang, J. Wang, Y. Sheng, W. Krolikowski, *Nat. Photonics* **2018**, 12, 591.
- [10] F. Chen, J. R. V. de Aldana, *Laser Photonics Rev.* **2014**, 8, 251.
- [11] A. Stone, M. Sakakura, Y. Shimotsuma, K. Miura, K. Hirao, V. Dierolf, H. Jain, *Mater. Des.* **2018**, 146, 228.
- [12] X. Huang, Q. Guo, D. Yang, X. Xiao, X. Liu, Z. Xia, F. Fan, J. Qiu, G. Dong, *Nat. Photonics* **2020**, 14, 82.
- [13] M. Xia, J. Luo, C. Chen, H. Liu, J. Tang, *Adv. Opt. Mater.* **2019**, 7, 1900851.
- [14] D. D. Hickstein, D. R. Carlson, H. Mundoor, J. B. Khurgin, K. Srinivasan, D. Westly, A. Kowligy, I. I. Smalyukh, S. A. Diddams, S. B. Papp, *Nat. Photonics* **2019**, 13, 494.
- [15] B. Zhang, L. Wang, F. Chen, *Laser Photonics Rev.* **2020**, 14, 1900407.
- [16] Y. Shimotsuma, P. G. Kazansky, J. Qiu, K. Hirao, *Phys. Rev. Lett.* **2003**, 91, 247405.
- [17] E. Bricchi, P. G. Kazansky, *Appl. Phys. Lett.* **2006**, 88, 111119.
- [18] Y. Shimotsuma, S. Kubota, A. Murata, T. Kurita, M. Sakakura, K. Miura, M. Lancry, B. Pommellec, *J. Am. Ceram. Soc.* **2017**, 100, 3912.
- [19] S. Richter, C. Miese, S. Döring, F. Zimmermann, M. J. Withford, A. Tünnermann, S. Nolte, *Opt. Mater. Express* **2013**, 3, 1161.
- [20] S. Richter, M. Heinrich, S. Döring, A. Tünnermann, S. Nolte, U. Peschel, *J. Laser Appl.* **2012**, 24, 042008.
- [21] F. Zhang, A. Cerkauskaite, R. Drevinskas, P. G. Kazansky, J. Qiu, *Adv. Opt. Mater.* **2017**, 5, 1700342.
- [22] B. Zhang, D. Tan, X. Liu, L. Tong, P. G. Kazansky, J. Qiu, *Adv. Opt. Mater.* **2019**, 7, 1900593.
- [23] Y. Shimotsuma, S. Mori, Y. Nakanishii, E. Kim, M. Sakakura, K. Miura, *Appl. Phys. A* **2018**, 124, 82.
- [24] J. Cao, L. Mazerolles, M. Lancry, D. Solas, F. Brisset, B. Pommellec, *Opt. Lett.* **2016**, 41, 2739.
- [25] E. Bricchi, B. G. Klappauf, P. G. Kazansky, *Opt. Lett.* **2004**, 29, 119.
- [26] X. Ma, Z. Peng, J. Li, *J. Am. Ceram. Soc.* **2015**, 98, 770.
- [27] A. Rosenflanz, M. Frey, B. Endres, T. Anderson, E. Richards, C. Schardt, *Nature* **2004**, 430, 761.
- [28] C. Joseph, P. Bourson, M. D. Fontana, *J. Raman Spectrosc.* **2012**, 43, 1146.
- [29] H. Ono, Y. Hosokawa, K. Shinoda, K. Koyanagi, H. Yamaguchi, *Thin Solid Films* **2001**, 381, 57.
- [30] P. S. Dobal, R. S. Katiyar, Y. Jiang, R. Guo, A. S. Bhalla, *J. Raman Spectrosc.* **2000**, 31, 1061.
- [31] K. Itoh, W. Watanabe, S. Nolte, C. B. Schaffer, *MRS Bull.* **2006**, 31, 620.
- [32] M. Sakakura, M. Shimizu, Y. Shimotsuma, K. Miura, K. Hirao, *Appl. Phys. Lett.* **2008**, 93, 231112.
- [33] V. Laguta, M. Buryi, M. Nikl, J. Zeler, E. Zych, M. Bettinelli, *J. Mater. Chem. C* **2019**, 7, 11473.
- [34] M. Buryi, J. Pejchal, V. Babin, M. Nikl, V. Laguta, *Phys. Rev. Appl.* **2018**, 10, 34058.
- [35] O. F. Schirmer, *J. Phys.: Condens. Matter* **2011**, 23, 334218.
- [36] M. Buryi, J. Rosa, D. Savchenko, J. Hybler, M. Nikl, S. Zazubovich, T. Kärner, C. R. Stanek, K. J. McClellan, V. V. Laguta, *Phys. Rev. B* **2014**, 90, 64104.
- [37] S. Richter, F. Jia, M. Heinrich, S. Döring, U. Peschel, A. Tünnermann, S. Nolte, *Opt. Lett.* **2012**, 37, 482.
- [38] M. Beresna, M. Gecevičius, P. G. Kazansky, T. Taylor, A. V. Kavokin, *Appl. Phys. Lett.* **2012**, 101, 053120.
- [39] D. Tan, X. Sun, Q. Wang, P. Zhou, Y. Liao, J. Qiu, *Opt. Lett.* **2020**, 45, 3941.
- [40] C. B. Schaffer, A. Brodeur, E. Mazur, *Meas. Sci. Technol.* **2001**, 12, 1784.
- [41] M. Gertsz, E. Simova, C. Hnatovsky, R. S. Taylor, V. R. Bhardwaj, D. M. Rayner, P. B. Corkum, P. P. Rajeev, *Phys. Rev. Lett.* **2006**, 97, 253001.
- [42] S. Nolte, U. Peschel, R. Buschlinger, *Phys. Rev. B* **2014**, 89, 184306.
- [43] J. Colombier, T. E. Itina, A. Rudenko, *Phys. Rev. B* **2016**, 93, 75427.
- [44] H. Wang, J. Song, Q. Li, X. Zeng, Y. Dai, *J. Phys. D: Appl. Phys.* **2018**, 51, 155101.
- [45] V. Oliveira, S. P. Sharma, P. Herrero, R. Vilar, *Opt. Lett.* **2013**, 38, 4950.
- [46] R. S. Taylor, C. Hnatovsky, E. Simova, P. P. Rajeev, D. M. Rayner, P. B. Corkum, *Opt. Lett.* **2007**, 32, 2888.
- [47] Y. Li, Y. Dou, R. An, H. Yang, Q. Gong, *Opt. Express* **2005**, 13, 2433.
- [48] Y. Shimotsuma, M. Sakakura, P. G. Kazansky, M. Beresna, J. Qiu, K. Miura, K. Hirao, *Adv. Mater.* **2010**, 22, 4039.